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NON-DESTRUCTIVE REACTIVATION OF CHEMICAL WARFARE PROTECTIVE GARMENTS
AND WRAPS

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PROJECT SUMMARY

In the near future, chemical protective combat uniforms will be worn by Army personnel on a continuous basis. Activated carbon, the operative component, is rendered useless upon exposure to dirt, smoke, sweat, and numerous other contaminants. Therefore, it is imperative to devise a method of laundering and reactivating the contaminated garments, which can be applied routinely without compromising the absorptive properties of the active carbon. The feasibility of non-destructive reactivation of the current protective material, a carbon impregnated foam, has been successfully demonstrated in the Phase I program. The method can be divided into a passive and an active regeneration phase. The passive regeneration phase involves three stages; first, a conventional laundering process to remove dirt, stain and water soluble contaminants, second, the treatment of the material with an effective displacing agent to facilitate the desorption of any remaining contaminants on the carbon surface, and third, the removal of the displacing agent by reduction and dissolution. The active regeneration phase involves the chemical activation of the carbon surface by means of energetic, electronically excited molecules.

Although the process has not been finalized, optimized nor completely understood, results obtained to date showed that close to 100% recovery of the carbon tetrachloride absorption capacity can be obtained by passive regeneration for carbon fabrics contaminated separately with detergent, simulated human sweat, cigarette smoke, engine exhaust fumes, petroleum products, transmission fluid and dirt. Approximately 80% recovery can be obtained when the fabric was contaminated with light oil by vacuum impregnation. Preliminary results showed that up to 140% recovery of the absorptive capacity can be achieved with combined passive and active regenerations.

Although the feasibility of non-destructive reactivation was demonstrated only with one material, the same process is expected to be applicable to carbon fibers or any other active-carbon-based materials with equal effectiveness. Successful implementation of the reactivation process will ultimately achieve enormous savings in chemical warfare defense.

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1.0 INTRODUCTION

In the near future, a single new uniform, the Chemical Protective Combat Uniform, will be used in lieu of both the Battle Dress Uniform and the chemical protective, Battle Dress Overgarment. As an essential requirement, this new uniform must be launderable, decontaminable and regenerable with little or no loss of chemical protective effectiveness. The primary goal of the present study lies in the development of non-destructive processes by which the active carbon uniform can be reactivated routinely.

The main objective of Phase I tasks is that of depositing separately, the various representative contaminants on fresh carbon material, applying the appropriate reactivation process for each contaminant, and conducting carbon tetrachloride tests to determine the recovered absorptive capacity. The various contaminated test samples will be subjected to a passive regeneration process aiming at the complete removal of contaminants from the carbon surface. Briefly, the method entails

(1) a conventional laundering process using non-phosphate deter-gent to remove dirt, stain and water soluble contaminants,

(2) an iodine treatment in conjunction with an aqueous and organic solvent to facilitate the desorption of contaminants. Iodine is used as an displacing agent to displace any remain-ing adsorbates on the carbon surface.

(3) an iodine removal cycle,

(4) a vacuum drying cycle which also facilitates removal of con-taminants through low boiling point, vacuum evacuation.

Although the passive regeneration method has not been completely finalized nor optimized, results obtained to date clearly demonstrated its effectiveness in removing various representative contaminants. Iodine staining of the non-active base cloth, foam substrract and the shell fabric does not appear to be a problem. No color change, nor degradation of strength and water repellency was observed following the regeneration process.

Early test results showed that some regenerated active carbon fabric exhibited a far better CCl_4 absorption capacity than that of a fresh sample. This anomaly had been investigated and it appeared to have been resolved. During the vacuum evacuation and drying process, the heat loss due to rapid evaporation was replenished by means of a microwave oven. The microwave energy which was originally intended merely to pro-vide heat may actually cause excitation of the electronic state of water molecules. These energetic steam or excited water molecules may in turn activate the carbon surface via a process very similar to the steam activation process commonly used in the production of active carbon. Electronic excitation, molecular dissociation and spontaneous plasma discharge are phenomena easily produced in a microwave oven under vacuum pressure. Vacuum drying with an infra-red lamp does not show any notice-able enhancement in absorptive activity.

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The accidentally discovered microwave enhancement effect has been studied. Preliminary results show that when applied to fresh carbon fabric, a 40% increase in CCl_4 absorption capacity can be achieved. It appears certain that it is possible not only to passively remove surface contaminants but also chemically "activate" the carbon material in an active sense.

2.0 METHOD AND PRINCIPLE

The primary goal of developing a non-destructive process for reactivation of chemical protective garments appears to be achievable. Results obtained to date clearly demonstrated the feasibility of using iodine as a displacing agent to facilitate the removal of representative contaminants from active carbon, even when such contaminants are applied to the utmost extent. Although only Type III material, an active carbon impregnated foam, was studied, the same process is expected to be applicable to carbon fibers or any other active carbon based materials with equal effectiveness.

2.1 Passive Regeneration - Removal Of Contaminants

Substances adsorbed on activated carbon are bonded to the microsurfaces by weak, Van der Waal forces. These substances can and do desorbed in a spontaneous fashion. The process of desorption of a certain substance can be accelerated by the introduction of another substance having a higher electrical polarizability. This more polarizable substance is called a displacing agent which competes with the original adsorbed species for the surface sites. Upon in contact with the activated carbon substrate, the molecule of the displacing agent is readily attached to the surface. Due to its high polarizability, this molecule alters the surface electrical potential distribution, weakens the attractive force between the substrate and the originally adsorbed molecules in its vicinity, and ultimately, causes these neighboring molecules to desorb from the activated carbon.

Iodine is the strongest displacing agent for activated carbon (REF. 1) and it can displace the most strongly held adsorbates. It can most effectively dislodge and desorb the following:

hydrocarbons	ketones	alcohols
ethers	halohydrocarbons	aldehydes
nicotine	carboxylic acids	carbon disulfide
phenols	organic nitro compounds	etc.

Because of this unique property, iodine was chosen as the displacing agent in the present application. Since an adsorbate can be displaced only into a solvent in which it is soluble, it may be more desirable to employ the iodine in solution in an organic solvent such as alcohols, xylenes, benzene, toluene, hexanes, halohydrocarbons and so on. Iodine dissolved in a 30/70 mixture of water and isopropyl alcohol appears to be a strong displacing agent for activated carbon.

For rejuvenation of activated carbon, the exact concentration of the iodine is not critical. However, a sufficient flow of iodine solution needs to be passed through the activated carbon to fully desorb the contaminants. A saturated solution of iodine in pure water at 25°C contains 0.34g per liter. With the addition of solubilizing salts, the dissolved

iodine can be substantially increased. In the extreme case of a saturated solution using potassium iodide as the solubilizing salt, the iodine, KI and water content are 67.8%, 25.6% and 6.6%, respectively. Manes (Ref. 1) suggested the use of a 0.1 N solution in aqueous potassium iodide, e.g., a solution containing 12.7 g of iodine and 40 g of potassium iodide in 1 liter of water. After a concentrated iodine/water solution is made, water and isopropyl alcohol can be added to obtain the desired mixture of iodine, water and isopropanol.

In a worst-case scenario, the garment is soiled, stained, covered with grease, contaminated by sweat, exhaust, fumes, solvents and hydrocarbons. As a first step, the dirt, stain, some grease and most water soluble contaminants will be removed by laundering the garment with detergent in a modified washing machine. After thorough rinsing, an iodine/water/isopropanol solution is introduced. Being the strongest displacing agent for carbon, iodine penetrates the various micro and macro pores, attaches to the carbon surface, and dislodges both weakly-and strongly-held adsorbates. No substantial amount of heel build-up is expected due to the unusual ability of iodine in lowering the surface energy and causing even the strongly-held adsorbates to desorb. Addition of isopropanol in the iodine solution substantially lowers the surface tension, thereby allowing the solution to penetrate small and deep pores readily.

After the displacement treatment, the iodine adsorbed on the carbon surface can be removed by washing in a dilute reducing solution containing one of the following reducing agents:

> potassium or sodium sulfite
> sulfurous acid
> stannous chloride
> potassium or sodium thiosulfate
> titanium trichloride

The iodides formed do not adsorb on the activated carbon. It is readily dissolved in water and can be washed away easily.

Finally, the wet garment can be spun dry in a conventional washing machine. The remaining water is then removed by vacuum evaporation. Even under "mild" vacuum pressure, the boiling point of water can be lowered drastically, and at room temperature, boiling, and therefore rapid evaporation, can occur. The heat of evaporation can be conveniently replenished by means of a low-duty-cycle, microwave oven. Alternatively, the heat can be supplied by an infra-red heat lamp. As discussed earlier, chemical activation (or reactivation) of the carbon can actually occur under certain conditions when microwave energy is utilized in the vacuum drying process. A discussion of the microwave activation phenomenon is presented in the next section.

2.2 Active Regeneration - Microwave Activation

Industrial processes used for manufacture of active carbons generally consist fo carbonization of the source material and activation with steam at elevated temperature (1600° - 2000° F). In vacuum drying the active carbon fabric, H_2O molecules evaporated may interact with the intense microwave field and adsorb a considerable amount of energy. These molecules in various excited energy states may have an equivalent, nonequilibrium temperature comparable to those used in the industrial steam activation process. It is believed that these energetic molecules can activate the carbon in a very similar manner.

A piece of dry active carbon fabric placed in a microwave oven does not adsorb any microwave energy. Whereas a piece of wet fabric will warm up gradually due to absorption of microwave energy by the water contained within. Only after complete evaporation and under vacuum can H_2O molecules accumulate sufficient energy to become excited, dissociated or even capable of sustaining a spontaneous plasma discharge at relatively moderate vacuum pressure ranges. By maintaining the carbon fabric at an appropriate vacuum pressure, in the presence of water vapor and microwave energy, a 40% increase in CCl_4 absorption capacity can be obtained with a fresh sample. Thus "chemical" activation of the active carbon by microwave excitation seems to have been confirmed. Besides, vacuum drying with an infra-red heat lamp did not produce the same effect.

Therefore, through proper implementation, the proposed non-destructive reactivation technique not only can remove surface contaminants in a passive sense via the iodine/solvent system, but also can "activate" the carbon surface in an active sense via microwave excitation involving H_2O molecules.

The energetic steam and excited H_2O molecules necessary for carbon activation can be conveniently obtained from a microwave source. Since the cost for a laboratory microwave generator with a sufficient power rating is prohibitively high, a commercially available microwave oven will be used in the present investigation.

As experimental setup adequate for the present feasibility study is schematically shown in Figure 1. The microwave enhancement system essentially consists of an industrial grade microwave oven, a vacuum test chamber, a pump, a pressure transducer, and arrangements for flow switching and control. Some of the relevant specifications of these equipment are summarized as follows:

    (1) Microwave Oven

        Manufacturer: Amana Refrigeration, Inc. Amana, Iowa
        Model: RR - 1110
        Frequency: 2450 MHz
        Microwave Power: 1000 Watts
        Electrical Rating: 110V and 20A
        Duty Cycle Control: 0 to 100% with a time base of 0.5 second
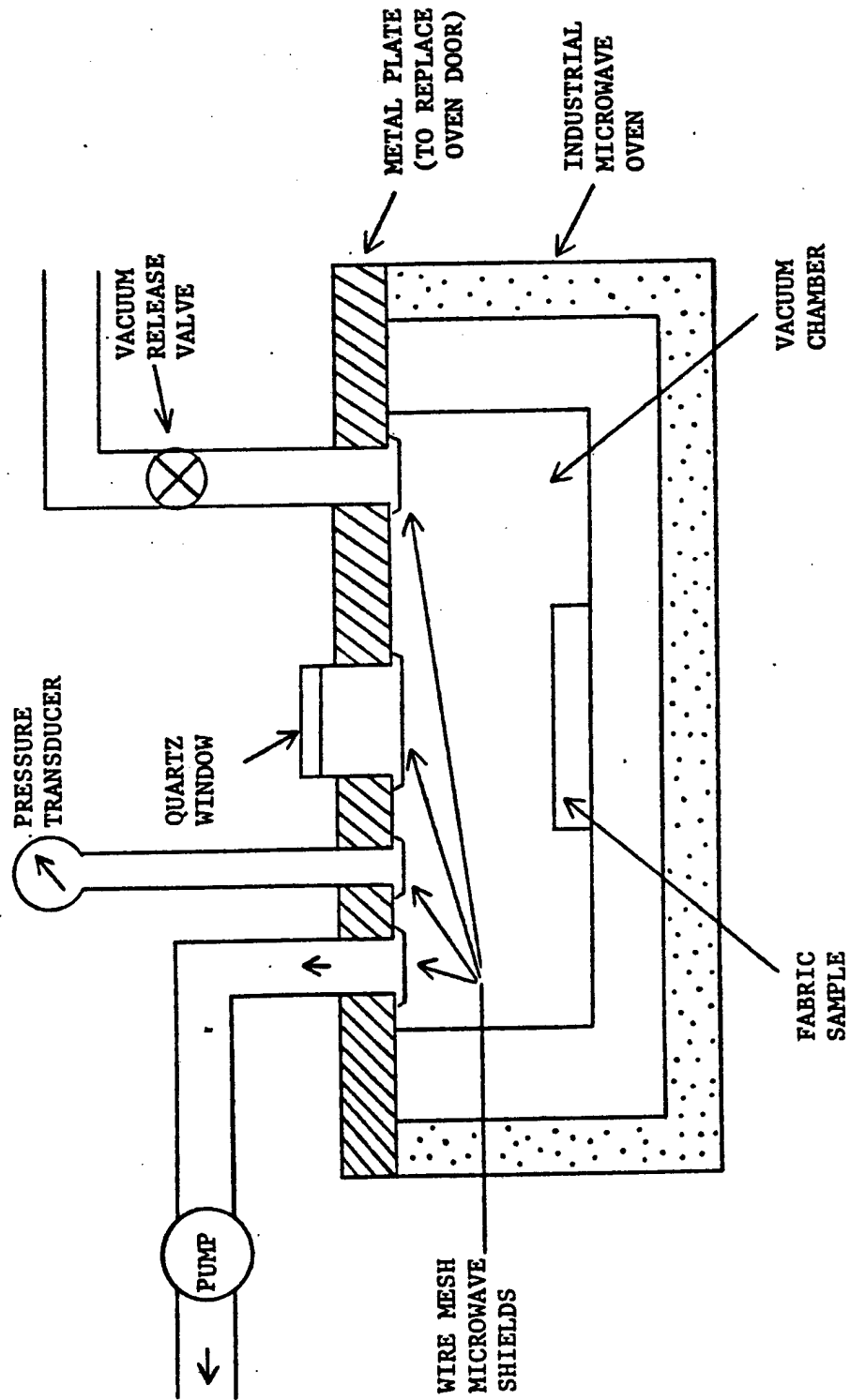   (minimum "ON" time per cycle)

FIGURE 1   SCHEMATIC DIAGRAM OF A MICROWAVE ACTIVATION SYSTEM

(2) Vacuum Pump

Manufacturer: Sargent-Welch Scientific Company, Skokie, Illinois
Model: 1402
Type: 2-stage rotary
Capacity: 160 liter per minute
Dead End Pressure: 1×10^{-4} Torr

(3) Vacuum Pressure Transducer

Manufacturer: Datametrics/Dresser Industries, Inc., Wilmington, Massachusetts
Model: 600 Barocel

(4) Vacuum Chamber

Manufacturer: Corning Glassworks, Corning, New York
Size: 4" I.D. x 6" O.D.
Material: Pyrex glass end cap

As depicted in Figure 1, the original door of the microwave oven is replaced by a ½ inch aluminum plate on which a small glass vessel (6" Pyrex end cap) is attached via a metallic clamping ring. Detachable couplers of gas inlet, pump outlet, pressure transducer, pressure gauge, and a quartz viewing window are all connected to the aluminum plate within the open area of the vacuum chamber. Fine copper screens of a mesh size comparable to that of the original door are installed on various inlet ports to prevent external leakage of microwave energy. In the absence of the original door, the concealed multiple safety interlocks must be by-passed before the microwave oven can be switched on. For the particular door design used in the Amana microwave oven, extra aluminum deflection plates must be installed around the oven to reduce microwave leakage through the gaps between the half-inch aluminum plate and the opening of the oven. The maximum leakage through the seams of the oven, the vacuum lines, and the viewing port was found to be well within the safety guideline established by the Federal Government (5 mW/cm^2 at a distance of 5 cm). The leakage energy was measured with a Model HI-1500 microwave survey meter manufactured by the Holaday Industries, Inc., Eden Prarrie, Minnesota. The chamber pressure is measured by means of a capacitance type Barocel pressure transducer.

2.3 Carbon Tetrachloride Absorption

The carbon tetrachloride activity of fresh and rejuvenated fabric samples can be determined by means of either a "DYNAMIC" or a "STATIC" CCl$_4$ absorption test.

2.3.1 Dynamic Test

The procedure and apparatus for a dynamic absorption test is described in REF. 2. Essentially, a 5 mg/liter carbon tetrachloride/nitrogen mixture equilibrated at 90° F is allowed to pass at a rate of 1 liter/minute through a sample cup where the test fabric is mounted. When the sample reaches its absorptive capacity, CCl$_4$ will penetrate the

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fabric and be detected downstream by a pyrolyzer and starch/iodide indicator solution. The CCl_4 absorption is proportional to the time delay of the appearance of carbon tetrachloride, and it can be expressed in weight per unit area when both the CCl_4 flow rate and area of the test sample are determined. The constant CCl_4 flow rate can be measured by a static absorption test where the weight gain per unit time of a tared, active-carbon-filled Schwartz tube is measured.

In the present study, a portable carbon tetrachloride absorption apparatus (Figure 2) was used in lieu of the standard apparatus for simplicity and efficiency. A stream of air maintained at 50 cc/min was bubbled through a CCl_4 solution at $0^\circ C$. The resulting stream becomes saturated with CCl_4 vapor. The partial pressure of CCl_4 is given by the following equation (REF. 5):

$$\log_{10} p = 8.004 - \frac{0.05223 \times 33914}{T}$$

Where p is the partial pressure in mmHg and T, the absolute temperature in $^\circ K$. Corresponding to $0^\circ C$, the CCl_4 partial pressure is calculated to be 33 mmHg, whereas the CCl_4 density is approximately 298 mg/liter. As shown in Figure 2, this air stream, which is saturated with CCl_4, is then diluted with another air stream maintained at 950 cc/min. Therefore, the total air flow is 1 liter/min and the CCl_4 flow is approximately 14.9 mg/min. The actual CCl_4 flow rate can be measured with a Schwartz tube filled with activated carbon.

The combined air stream is allowed to pass through the sample cup and the penetration of CCl_4 is detected by a propane halide detector. When the fabric sample reaches its maximum absorptive capacity, carbon tetrachloride will pass through and be detected by the halide detector as indicated by a green flame. The elapsed time from the instant sample cup is attached to the end point when green flame appears is a measure of the CCl_4 absorption activity of the fabric.

2.3.2 Static Test

The static absorption test uses the same apparatus (Figure 2) except that the halide detector is no longer used. The air stream contianing 14.9 mg/liter of CCl_4 is allowed to pass through the fabric sample maintained at room temperature until there is no further increase in the weight of the fabric. The percentage increase in the weight of the carbon fabric is the carbon tetrachloride absorption activity.

Generally speaking, the dynamic test is more time consuming, requires frequent calibration and flow adjustment, and the result is less reproducible even with fresh uncontaminated samples. Although the dynamic test provides a measurement more accurately reflecting the efficacy of the active carbon fabric in so far as personnel protection is concerned, it is affected more by pinholes, nonuniformity of the fabric, and the inaccuracy in detecting the onset of the green flame. For preliminary screening tests, the main concern and interest lies in the recovery of absorptive capability of active carbon, a static test appears to be more efficient and appropriate. The advantages of static absorption test are:
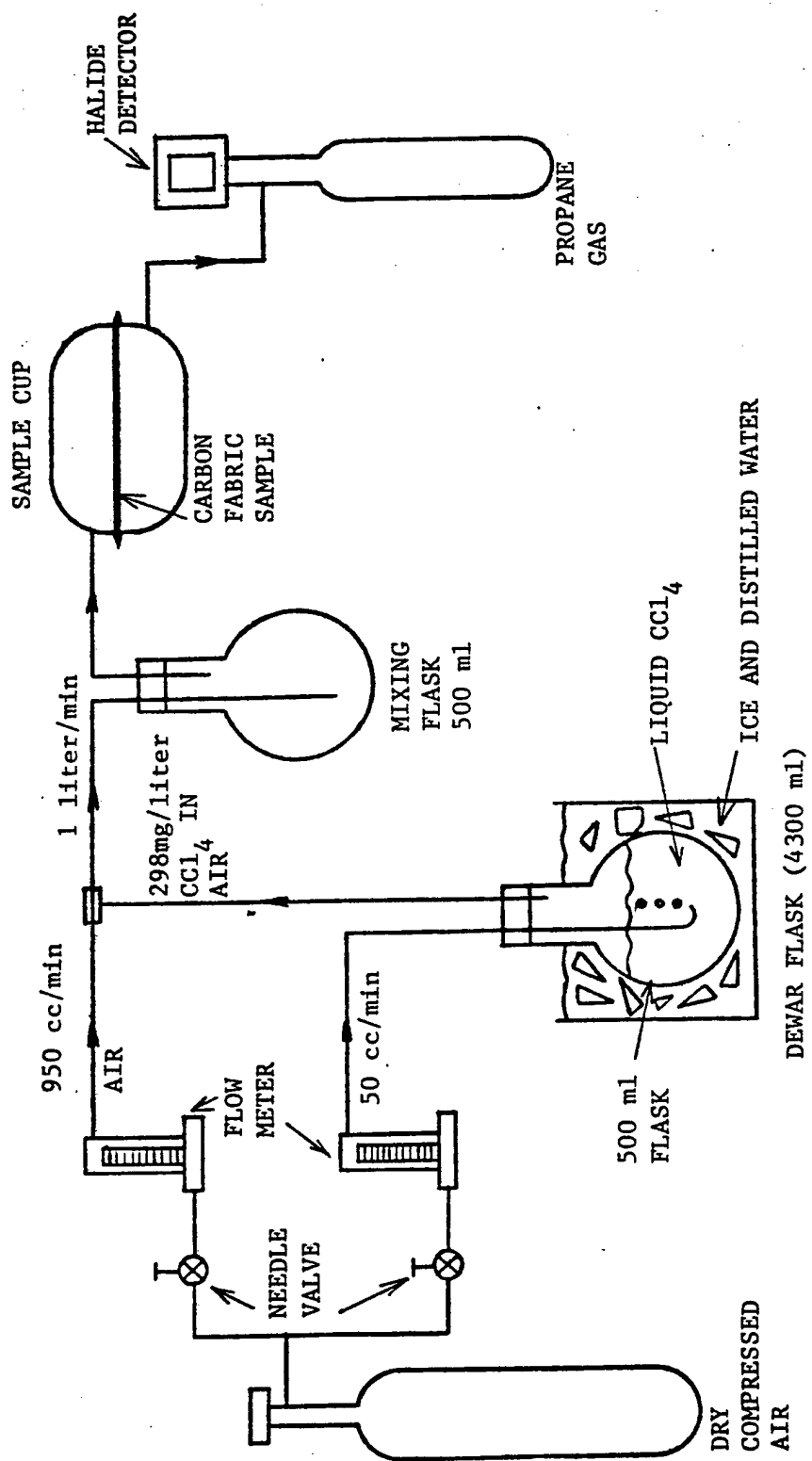
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FIGURE 2   SIMPLIFIED CCl₄ PENETRATION APPARATUS FOR DYNAMIC ABSORPTION TEST

(1) it yields more reproducible results,

(2) it is more efficient and less time consuming.

(3) it is less sensitive to CCl_4 flow rate,

(4) it is not sensitive to the presence of pinholes, non-uniformity and loss of carbon particles due to handling and washing,

(5) it allows testing of several samples simultaneously.

For these reasons, the majority of tests were conducted by using the static absorption method. Although, in general, the CCl_4 absorption per unit area (or per unit weight) based on the static test was found to be slightly higher than that associated with the dynamic test, both methods yield data which appears to be essentially consistent and equivalent.

3.0 EXPERIMENTAL PROCEDURE AND RESULTS

The chemical protective garment is assumed to be composed of an outer, camouflage Shell Fabric and an inner foam laminate containing active carbon. The relevant specifications are summarized as follows:

(1) Shell Fabric
   Document: MIL-C-44031A, 30 December 1982
   Title: Cloth, Camouflage Pattern: Woodland, Cotton and Nylon
   Description: NYCO camouflage fabric, Quarpel-treated, Class II
   Weight: 7.0 ounces per square yard, minimum

(2) Foam Laminate
   Document: MIL-C-43858A (GL), 7 May 1984
   Title: Cloth, Laminated, Nylon Tricot Knit, Polyurethane Foam
          Laminate, Chemical Protective and Flame Resistant
   Description: Type III material, activated carbon with an
               average particle size of 15 microns
   Weight: 7.5 - 9.5 ounces per square yard
   Thickness: 0.070 - 0.110 inches
   Carbon Tetrachloride Absorption (REF. 2): 1.8 mg/cm^2 minimum
   Base Cloth: Tricot knit nylon, 1.8 - 2.2 ounces per square yard
   Foam: Polyurethane, 0.089 - 0.109 inches thick, 2.0 lbs/cubic
         feet maximum

Although only Type III material was used in the current study, the same process and results are expected to be applicable to carbon fibers or any other active-carbon-based materials including those used in patient wraps.

Finally, some of the relevant measurements of the actual Type III material used in the present study are:

Average Weight: 0.03 gm/cm^2 (8.8 ounce/sq. yard)
Average Thickness: 0.25 cm (0.10 inch)
Estimated Weight of Active Carbon* : 0.015 gm/cm^2

3.1 Passive Regeneration

3.1.1 Experimental Method

The primary tasks of the Phase I program can be briefly summarized as follows:

(1) Controlled Contamination - various representative contaminants are separately deposited on fresh carbon foam material in a controlled, reproducible manner.

(2) Passive Reactivation - various contaminants are removed by the combined process involving detergent wash, iodine/water/organic solvent wash, iodine removal, and vacuum evacuation (drying).

(3) CCl$_4$ Absorption Test - the efficacy of the passive reactivation process was evaluated by means of the standard CCl$_4$ absorption test.

In applying the various contaminants to the active carbon foam material, complete saturation and full coverage of the contaminants was

* Based on a thickness of 0.25cm, total fabric weight of 0.03gm/cm^2, weight of base cloth, 0.007gm/cm^2 (2 ounces/sq.yd), and weight of foam 0.032gm/cm^3 (2 lb/ft^3).

attempted in all cases. As a result, the active carbon material was always contaminated in a manner far more severe than expected in real life.

The various representative contaminants chosen are:

(1) detergent
Type II non-phosphate detergent (REF. 3)

(2) simulated human sweat (REF. 4)
300 mg% sodium chloride
90 mg% potassium chloride
230 mg% lactic acid
15 mg% urocanic acid
62 mg% urea
19 mg% citrulline
72 mg% serine
37 mg% alanine
156 mg% leucine
balance water

(3) cigarette smoke
Camel brand cigarette (filterless)

(4) engine exhaust
gasoline engine

(5) petroleum products
50/50 mixture of no lead gasoline and diesel fuel

(6) light lubricating oil
Mobil SF10A4

(7) dirt
a slurry of garden soil

(8) transmission fluid
Mobil ATF 220

In order to ensure complete contamination, detergent solution, simulated sweat, oil, transmission fluid and dirt slurry were applied to the active carbon by vacuum impregnation. Full contamination of cigarette smoke and engine exhaust was accomplished by prolonged exposure to high concentration within a closed chamber. Due to its low surface tension, petroleum fuel mixture was applied directly by soaking.

The liquid phase regeneration process generally entails the following steps:

(1) immerse in water and apply vacuum pressure to remove air within contaminated carbon fabric,

(2) launder in 1.25% Type II non-phosphate detergent at 90°F,

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(3)   rinse in 90°F water,

(4)   transfer laundered sample piece into a 0.1N iodine/water/ isopropanol solution maintained approximately at 90°F,

(5)   rinse in water,

(6)   transfer sample piece into a 90°F 0.1N solution of sodium thiosulfate,

(7)   rinse in 90°F water,

(8)   squeeze out excess water and allow the test fabric to dry in a vacuum chamber maintained at mild vacuum,

(9)   replenish heat of evaporation via an infra-red heat lamp controlled by a variac transformer.

Since discovery of the microwave enhancement effect, the vacuum drying process was used only in conjunction with a heat lamp so that only the effect of "passive reactivation" is evaluated. The effect due to microwave enhancement was studied separately.

The regenerated test samples were then evaluated by both "dynamic" and "static" CCl_4 absorption tests. The dynamic test utilizes a portable type CCl_4 Absorption Apparatus to obtain a constant CCl_4 flow rate and a propane halide detector to detect the appearance of CCl_4 in the flow stream. The static test uses the same apparatus but records only the percentage weight increase after total saturation. Although the CCl_4 absorption per unit area (or per unit weight) based on the static test was found to be higher than that associated with dynamic test, both methods yield data which appears to be essentially consistent and equivalent. The static test method was found to be more efficient, less time consuming, less sensitive to pinholes, non-uniformity, and carbon loss, and it allows testing of several samples simultaneously. The static test has been conveniently and effectively used in most preliminary tests.

3.1.2 Descriptive Findings

DETERGENT RESIDUES

As a first step in garment regeneration, detergent solution will be used to launder out stains, grease, dirt, sweat residues and other contaminants. In order to ensure that the detergent solution does not poison active carbon, the Type II non-phosphate detergent was initially treated as a polluting agent. Test results based on both dynamic and

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static CCl$_4$ absorption tests showed that the Type II detergent, as expected, does not poison the active carbon.

HUMAN SWEAT RESIDUES

Because the simulated sweat solution does not penetrate the carbon material readily, full contamination was achieved by vacuum impregnation. Test results show that complete regeneration can be achieved with either detergent wash, aqueous iodine solution or iodine/water/isopropanol mixture.

CIGARETTE SMOKE

Complete contamination was believed to have achieved by prolonged exposure of the carbon fabric to cigarette smoke in a closed container. The fabric samples were placed 2" above burning cigarettes. Air was allowed to enter through a small opening to sustain burning. Fresh cigarettes were frequently replaced and samples were removed from the container after 1 hour.

Initial CCl$_4$ absorption showed that both detergent wash and iodine soaking failed to regenerate the carbon fabric to any substantial extent. Strong cigarette odor can still be detected following the reactivation process. It was suspected that water insoluble substances may have been deposited on the active carbon, which rendered the displacing agent (i.e., iodine) less effective.

Because an adsorbate can be displaced only into a solvent in which it is soluble, the aqueous iodine solution was replaced in subsequent tests by an iodine/water/organic solvent system containing 0.1N iodine in 30% water and 70% isopropyl alcohol by volume. As a result, close to complete regeneration of the active carbon can be achieved, and no cigarette odor can be detected.

PETROLEUM PRODUCTS

A 50/50 mixture of no lead gasoline and diesel fuel was chosen as a representative petroleum product. Due to its low surface tension, this contaminant was directly applied by soaking. As is expected, both detergent and iodine solution have little or no effect on the petroleum mixture and strong odor lingered on despite repeated washing.

Again, dramatic improvement was obtained with the use of the iodine/water/isopropanol mixture, and close to full regeneration appeared to have achieved. The previously lingering petroleum odor disappeared altogether with just a few short wash cycles.

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LUBRICATING OIL

Although neither heavy nor light oil can penetrate the outer fabric (NYCO camouflage fabric, Quarpel-treated), light lubricating machine oil was still used as a test contaminant. Vacuum impregnation was applied to ensure complete fouling of the carbon fabric. Because of the amount of oil the fabric contained, it was pointless to wash the fabric sample in water. Therefore, iodine/water/isopropanol mixture was used to wash out the excess oil first before initiation of the detergent wash.

Based on visual inspection, detergent wash appeared to be ineffective in removing even surface oil stains despite prolonged washing. Only partial (approximately 80%) regeneration can be achieved with either iodine/water/ isopropanol mixture or perchloroethylene wash.

ENGINE EXHAUST FUMES

Contamination of carbon fabric by engine fumes was accomplished by means of a pressure pump which withdrew exhaust fumes into a closed chamber from inside the tail pipe of a gasoline car engine via a long Teflon tube. The engine was raced once every 5 minutes to ensure the supply of hydrocarbon pollutants. The total exposure time was approximately 30 minutes.

It was found that substantial regeneration can be achieved with iodine/water treatment and close to full regeneration was obtained with iodine/water/isopropanol.

DIRT

"Dirt" contamination was simulated by a slurry of ordinary garden soil. Regeneration with aqueous iodine solution appeared to be adequate. Again, full regeneration was observed with either aqueous iodine solution or an iodine/water/isopropanol mixture.

TRANSMISSION FLUID

The effect of transmission fluid on the carbon fabric is very similar to that of light lubricating oil. Partial regeneration (approximately 65%) can be achieved with iodine/water/alcohol wash and close to full regeneration can be achieved with percholoroethylene wash.

3.1.3 Static Test Results

This section presents test data obtained via the static CCl_4 absorption technique. Due to the unavoidable and uncertain loss of active carbon during washing and handling, the data were normalized by total weight of the carbon fabric rather than by area. The various test data are summarized in the following table:

Contaminant	Treatment	CC1$_4$ Absorption (per unit fabric weight) (%)	Standard Deviation (%)	MAX./MIN. (%) (%)
None	None	12.3	1.5	14.6/9.54
None	Vacuum	14.5	1.6	17.0/12.4
Detergent	Vacuum	14.2	1.4	16.2/12.1
Sweat	Vacuum	9.6	1.2	11.2/8.2
Sweat	Iodine/Water/Isopropanol Vacuum	14.8	1.4	16.5/12.9
Cigarette Smoke	None	8.4	1.0	9.5/7.2
Cigarette Smoke	Iodine/Water/Isopropanol Vacuum	14.1	1.5	16.1/11.8
Engine Exhaust	None	9.0	1.9	11.2/6.0
Engine Exhaust	Iodine/Water/Isopropanol Vacuum	15.8	1.5	17.4/13.8
Petroleum Products	Iodine/Water/Isopropanol Vacuum	13.6	0.6	14.1/12.4
Oil	Iodine/Water/Isopropanol Vacuum	10.2	2.1	13.2/6.5
Oil	Perchloroethylene Vacuum	11.8	0.5	12.4/11.2
Dirt	Iodine/Water/Isopropanol Vacuum	15.5	1.9	18.4/13.2
Transmission Fluid	Iodine/Water/Isopropanol Vacuum	11.5	1.1	12.3/9.6
Transmission Fluid	Perchloroethylene Vacuum	14.6	0.9	16.1/13.8

Despite the scatter in experimental data which is largely attributed to the uncertain loss of carbon particles, it appears that the removal of contaminants can, by and large, be achieved with passive regeneration even when the various representative contaminants were applied to the utmost extent in each case. For oil and transmission fluid, full recovery of the absorption capacity may still be achievable if extra time were allowed to thoroughly wash out the remaining residues within the deep carbon pores. In any case, this extra washing is not needed because in a practical situation, the oil and transmission fluid seldom contaminate the active carbon garment to such an extent. Perchloroethylene, the common solvent used in commercial dry cleaning, appears to be more effective in removing oil and transmission fluid. Therefore, a perchloroethylene pre-wash cycle may be employed when the garment is heavily contaminated with oil, trasmission fluid and the like.

As mentioned previously, the various contaminants were applied to the active carbon fabric in a manner much more severe than expected in real life. Regeneration of carbon fabric samples exposed to certain pollutants under more realistic test conditions was also investigated. Identical samples exposed to the atmosphere in an office environment for approximately four weeks were studied and the results are:

Contaminants	Treatment	CCl_4 Absorption (per unit fabric weight) (%)
Office Air	None (dehumidified)	9.5
Office Air	None (dehumidified)	11.4
Office Air	Isopropanol Rinse Vacuum Evacuation	15.5
Office Air	Isopropanol Rinse Vacuum Evacuation	13.8
Office Air	Iodine/Water/Isopropanol Vacuum Drying	14.8
Office Air	Iodine/Water/Isopropanol Vacuum Drying	13.6

The untreated samples were dehumidified in a desiccator before undergoing the static absorption test to avoid dissolution of CCl_4 in water. These preliminary test results indicated that the contaminated samples can readily be regenerated even with an isopropanol rinse and vacuum evacuation. However, the role of iodine can not be diminished because in the case of cigarette smoke and petroleum products contamination, the smell of contaminants are completely removed following iodine treatment whereas even prolonged vacuum evacuation failed to eliminate the odors of cigarette and fuels.

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3.1.4 Dynamic Test Results

This section presents the test data obtained via the dynamic test method using a propane halide detector to sense the initial penetration of CCl_4.

Contaminant	Treatment	CCl_4 Absorption (mg/cm^2)	Average (mg/cm^2)
None	None	2.45	
		2.08	
		2.15	2.23
None	Vacuum Evacuation	2.61	
		2.44	
		2.56	2.54
Detergent	Water Rinse	2.74	
	Vacuum Evacuation	2.31	
		2.48	2.51
Sweat	Vacuum Evacuation	2.07	
		1.81	
		1.72	1.87
Sweat	Iodine/Water/Isopropanol	2.70	
		2.56	
		2.33	2.53
Cigarette Smoke	None	1.86	
		1.54	
		1.08	1.49
Cigarette Smoke	Iodine/Water/Isopropanol Vacuum Evacuation	2.60	
		2.23	
		2.28	2.37
Engine Exhaust	None	2.20	
		1.88	
		1.64	1.91
Engine Exhaust	Iodine/Water/Isopropanol Vacuum Evacuation	2.77	
		2.39	2.58
Petroleum Products	None	Not Tested	

Contaminant	Treatment	CCl_4 Absorption (mg/cm^2)	Average (mg/cm^2)
Petroleum Products	Iodine/Water/Isopropanol	2.68 2.08	2.38
Oil	None	Not Tested	
Oil	Iodine/Water/Isopropanol Vacuum Evacuation	2.08 1.78 1.88	1.91
Oil	Percholoroethylene Vacuum Evacuation	2.14 2.08	2.11
Dirt	None	2.02	2.02
Dirt	Iodine/Water/Isopropanol Vacuum Evacuation	2.78 2.43 2.20	2.47
Transmission Fluid	None	Not Tested	
Transmission Fluid	Iodine/Water/Isopropanol Vacuum Evacuation	2.14 1.99	2.06
Transmission Fluid	Percholoroethylene Vacuum Evacuation	2.23	2.23

3.2 Active Regeneration

As discussed in Section 2.2, the active carbon fabric can be "chemically" activated by means of a microwave excited steam under low pressure (vacuum) conditions.

The feasibility of chemical activation, microwave enhancement and vacuum drying of active carbon fabric can be demonstrated with the simple setup shown in Figure 1. A wetted fabric sample, fresh or passively regenerated, placed in the test chamber will warm up gradually due to absorption of microwave energy by the water contained within. The duty cycle of the microwave oven is generally set at the minimum 10% to avoid overheating. As a result, one (1) kilowatt of microwave power is applied for a duration of 0.5 second once every 5 seconds. Although the temperature of the fabric sample remains low, rapid evaporation occurs due to the drastic reduction of the boiling point under vacuum. The chamber pressure remains high (greater than 100 Torr.) as long as there is liquid water remaining in the fabric. Within a few minutes, the pressure drops below 100 Torr. and the fabric is essential dry. The chamber is filled with water vapor (or steam) at vacuum pressure. Under this condition, the H_2O molecules can absorb an enormous amount of microwave energy and enter into a spontaneous, intense plasma discharge. This plasma discharge manifests itself by giving off an intensive light emission. The plasma discharge can be suppressed by controlling the chamber pressure.

Since a relatively low temperature (1600° - 2000° F) is generally used for steam activation in the manufacture of active carbon, extremely energetic steam such as that generated by a H_2O plasma discharge is not required. Therefore, in the present application, active regeneration is carried out at a higher pressure (2 to 10 Torr., approximately) where plasma discharge is suppressed.

Despite the presence of high energy steam, thermal degradation of the nylon base cloth and polyurethane foam substrate was not observed due to the following reasons:

(1) In microwave excitation of steam under mild vacuum, the translational energy or, thermodynamic temperature is expected to be low as compared to its nonequilibrium temperature. In other words, the steam is energetic in terms of chemical activity (in an excited state) but "cold" in the conventional sense.

(2) The bulk temperature rise is small due to the "thinness" of the steam and the low pressure (2 to 10 Torr.).

(3) Low duty cycle (10%) activation.

Even in the extreme case when H_2O plasma discharge was allowed to appear, there was no visible sign of burning or thermal degradation. However, at high pressure (1 atm.) and high duty cycle (100%), a fabric sample will be destroyed in a few minutes, not because of H_2O plasma discharge but due to uncontrolled heating.

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3.2.1 Static Test Results

Fresh and passively regenerated carbon fabrics were subjected to active regeneration under microwave excitation. The preliminary test results are summarized as follows:

Contaminant	Treatment	CCl_4 Absorption (per unit fabric weight) (%)	Standard Deviation (%)	MAX./MIN. (%) (%)
None	None	12.3	1.5	14.6/9.54
None	Vacuum	14.5	1.6	17.0/12.4
None	Active Regeneration	22.2	0.6	23.1/21.6
Cigarette Smoke	Iodine/Water/Isopropanol Active Regeneration	18.5	0.6	19.4/18.0
Exhaust Fumes	Iodine/Water/Isopropanol Active Regeneration	21.8	1.0	22.8/20.4

3.2.2 Dynamic Test Results

Fresh samples of the active carbon foam fabric were activated by means of microwave excitation. The test results are:

Treatment	CCl_4 Absorption (mg/cm^2)	Average (mg/cm^2)
None	2.45	
None	2.08	
None	2.15	2.23
Vacuum Evacuation	2.61	
Vacuum Evacuation	2.44	
Vacuum Evacuation	2.56	2.54
Microwave Activation	3.69	
Microwave Activation	3.40	
Microwave Activation	3.36	3.48

3.3 Shell Fabric

Due to its excellent hydrophobicity and water repelling property, the outer fabric of the protective garment (NYCO camouflage fabric, Quarpel-treated) is safe from staining by aqueous iodine solution. When iodine/water/isopropanol was used, dark yellow stain appeared on the fabric surface. However, this iodine stain disappeared instantly and completely upon washing in a sodium thiosulfate solution. Colorfastness to the

reducing solution was observed and there was no observable degradation
in hydrophobicity.

4.0 DISCUSSIONS

The primary goal of developing a non-destructive process for reactivation of chemical protective garments appears to be achievable. Results obtained to date clearly demonstrated the feasibility of using iodine, a strong displacing agent for the removal of contaminants, isopropanol, a common organic solvent, to remove water insoluble contaminants, a vacuum process to evacuate the micro-pores, and microwave excited steam to chemically reactivate the active carbon. Although only Type III material was studied, the same process is expected to be applicable to carbon fibers or any other active-carbon-based materials with equal effectiveness. Iodine staining of the shell fabric of the garment does not appear to be a problem and no color change nor degradation of water repellency was observed following the regeneration process.

To recapitulate, the processes under current study were divided into passive and active regeneration. Passive regeneration refers to processes designed solely to remove contaminants from the carbon surface. Active regeneration refers to processes which can result in chemical activation of the carbon material. Following passive regeneration alone, close to 100% recovery of the CCl_4 absorption capacity was obtained for active carbon fabrics contaminated separately with detergent, simulated human sweat, cigarette smoke, engine exhaust fumes, petroleum fuels, oil, transmission fluid, and garden soil. With a combined passive and active regeneration, up to 140% recovery of the original CCl_4 absorption activity can be achieved. An approximately 40% enhancement in CCl_4 absorption can be obtained with fresh active carbon fabric after active regeneration.

The problems encountered in the present study are:

(1) Carbon Loss

Despite the various binders used in the manufacture of the Type III material, appreciable carbon loss can occur during washing, handling and testing.

(2) Pressure Control

Capability for precise pressure control, which is essential to the active regeneration process, was lacking with the microwave/vacuum system used in the present study. A servo valving system is needed to bleed in steam and maintain a preset vacuum pressure.

(3) Displacing Effect of CCl_4

The presence or absence of displacing effect due to CCl_4 is unknown. Carbon tetrachloride has been used extensively for evaluation of largely fresh uncontaminated active carbon material. However, it is conceivable that like iodine, CCl_4 may act as a displacing agent which tends to desorb contaminants originally on the carbon surface and be adsorbed on the same site. This effect if present may explain the unexpected degree of CCl_4 absorption of seemingly contaminated

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fabric samples.

 (4) Controlled Contamination

  It is difficult to devise a method of controlled contamination which is practical, reproducible, and truely representative of the extent of contamination to be encountered in actual combat environment.

Finally, it should be emphasized that the reactivation of active carbon material was made possible by the following effective techniques:

 (1) utilization of iodine, the strongest displacing agent

 (2) use of aqueous and organic solvents

 (3) use of vacuum evacuation

 (4) use of energetic, microwave excited steam for chemical activation

and for implementation of these techniques and processes, only simple, commercially available equipment will be required.

5.0 REFERENCES

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